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LUBRICATING PROPERTIES OF SOME BONDED FLUORIDE AND

OXIDE COATINGS FOR TEMPERATURE TO 1500° F

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SUMMARY

The lubricating properties of some experimental ceramic coatings, diffusion-bonded fluoride coatings, and ceramic-bonded fluoride coatings were determined. The experiments were conducted in an air atmosphere at a sliding velocity of 430 feet per minute and at temperatures from 75° to 1500° F.

Several ceramic coatings provided substantial reductions in friction coefficient and rider wear (compared with the unlubricated metals). For example, a cobaltous oxide (CoO) base coating gave friction coefficients of 0.24 to 0.36 within the temperature range of 75° to 1400° F; serious galling and welding of the metal surfaces were prevented. The friction coefficients were higher than the arbitrary maximum (0.2) usually considered for effective boundary lubrication. However, when a moderately high friction coefficient can be tolerated, this type of coating may be a useful antiwear composition. Diffusion-bonded calcium fluoride (CaF_2) on Haynes Stellite 21 and on Inconel X gave friction coefficients of 0.1 to 0.2 at 1500° F. Endurance life was dependent on the thermal history of the coating; life improved with increased exposure time at elevated temperatures prior to running. Promising results were obtained with ceramic-bonded CaF_2 on Inconel X. Effective lubrication and good adherence were obtained with a 3 to 1 ratio of CaF_2 to ceramic. A very thin sintered and burnished film of CaF_2 applied to the surface of this coating further improved lubrication, particularly above 1350° F. The friction coefficient was 0.2 at 500° F and decreased with increasing temperature to 0.06 at 1500° F. It was 0.25 at 75° F and 0.22 at 250° F.

A survey of the thermochemical properties of the halides was of considerable aid in selecting metal halides that might be chemically stable in air at 1500° F. Good correlation was obtained between predictions based on thermodynamics and the results of experimental thermal stability studies.

INTRODUCTION

High-temperature lubrication is a problem area in which the use of bonded solid lubricants has been of considerable value. At about 500° or 600° F most oils and greases show considerable oxidative or thermal degradation; therefore, other types of lubricants are required.

A present design trend is to circumvent the high-temperature lubrication problem by cooling the bearing surfaces or locating them at a considerable distance from heat sources. Considerable simplification of components and savings in space and weight would be derived by eliminating auxiliary cooling and by locating bearings as close to heat sources as an optimum mechanical design would dictate. In many applications, this could be accomplished if a bonded solid lubricant with good thermal stability at temperatures of 1000° F and higher were used. This approach appears especially appropriate in the design of components for space vehicles and aircraft in which weight savings are important.

A research program on high-temperature dry film lubricants has been conducted at the NASA Lewis Research Center. Ceramic coatings have been the subject of considerable interest. In particular, compositions based on lead monoxide (PbO) have shown considerable promise for use at temperatures up to 1250° F (ref. 1).

The objective of the research reported herein was to explore the feasibility of various oxide and halide coatings for use as dry film lubricants at temperature to 1500° F. It was required that the coatings be stable in air and of low volatility to 1500° F. These requirements were imposed with the objective of developing lubricants that would be effective over a large range of temperatures and altitudes. At low altitudes (high oxygen partial pressure), oxidative stability is necessary; at high altitudes (low oxygen partial pressure), vaporization rates become important.

The report includes a description of a screening method, based on thermodynamic concepts, that was employed in selecting metal halides for study as experimental high-temperature solid lubricants. The correlation obtained between thermodynamic predictions and empirical thermal stability data is reported. The formulation, application, and lubricating properties of three types of coating (ceramic, ceramic-bonded fluoride, and diffusion-bonded fluoride) are described.

SELECTION OF MATERIALS

The first criterion used for selecting materials was good chemical stability in air at 1500° F. It was further required that the materials have a low vapor pressure at 1500° F, in order to ensure retention of the solid on the surfaces requiring lubrication. (A low vapor pressure would not necessarily be required in sealed systems or in systems for which the supply of lubricant could be continuously replenished.) Other properties of importance are high melting point, low water solubility (when storage in moist atmospheres is likely), and crystal properties that are conducive to a low friction coefficient, such as the presence of easily sheared lattice planes.

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The chemical stability of halides in air can be estimated from their thermochemical properties, particularly from the free-energy changes involved in the decomposition of the halide to form the corresponding oxide. A typical reaction of this type is:

$$MX_2 + \frac{1}{2} O_2 = MO + X_2 \tag{1}$$

where M represents any divalent metal ion, and X represents any halide ion.

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The mathematical expression used in calculating free-energy change for (1) is

$$\Delta F_T = \Delta F_T^o + 2.3\ RT \log \frac{P(X_2)}{\left[P(O_2)\right]^{1/2}} \tag{2}$$

where

R universal gas constant

T absolute temperature, ^oK

$P(X_2)$ partial pressure of halogen gas, mm Hg

$P(O_2)$ partial pressure of oxygen, mm Hg

ΔF_T free energy of reaction at a specified temperature (T) and specified partial pressures of halogen gas and oxygen, cal/g at. wt.

ΔF_T^o standard free energy of reaction at a specified temperature (Standard free energy of reaction applies to a reference state in which the partial pressures are equal to unity. This gives a logarithmic term in eq. (2) that is equal to zero; i.e., $\Delta F_T = \Delta F_T^o$. For all other partial pressures, the logarithmic term supplies the necessary correction for calculating a free energy of reaction applicable to the specific pressures involved.)

A positive ΔF_T indicates that the reaction will not proceed to the right, and conversion to the oxide cannot occur under the specific conditions assumed in the calculations. A negative ΔF_T indicates the oxide is more stable than the halide and the reaction may proceed to the right. Whether or not this occurs and, if so, at what rate, cannot be predicted by thermodynamics. However, it is indicated that the potential for reaction exists; and, at elevated temperatures in particular, an appreciable reaction rate is likely.

The standard free energies of formation for halides and oxides from references 2 and 3 were used in calculating the standard free energies of reaction given in figure 1. This figure gives the effect of temperature on ΔF_T^o for the conversion of a number of metal halides to the corresponding oxides. The order in which the curves appear gives a direct indication of the relative oxidative stabilities of the halides at a standard reference state. When the partial pressures of halogen gas and oxygen are not unity, the curves are translated along the vertical axis, but their relative positions remain unchanged for any given value of the ratio $p(X_2)/[p(O_2)]^{1/2}$.

In the reference state, all of the fluorides are stable with respect to the corresponding oxides. Iron, cobalt, and nickel chlorides become unstable at about 1500° F; the bromides and iodides are thermodynamically unstable over the entire temperature range. (The apparent stability of iron-group bromides and iodides at room temperature is attributable to an extremely low reaction rate or a high activation-energy requirement for conversion to the oxide.) However, at elevated temperatures in air the iron, cobalt, and nickel chlorides, bromides, and iodides can be expected to decompose to the oxide at an appreciable rate.

To test these conclusions, experiments were conducted in which the thermal stabilities of some of the metal halides were studied. The results are given in table I. The compounds were heated in open air for 1 hour at the temperatures indicated, and X-ray diffraction studies were made of the reaction products. The compounds are arranged in the table in the order of decreasing stability. Good agreement exists between the experimentally determined order given here and the order predicted by the thermodynamic data of figure 1. SrF_2 and CaF_2 were not converted to oxides at temperatures up to 2000° F.

Although iron, cobalt, and nickel halides decompose in air at elevated temperatures, they are stable in halogen-rich atmospheres. Nickel bromide ($NiBr_2$) and cobalt chloride ($CoCl_2$), in particular, have shown much promise in reactive gas lubrication (ref. 4). In this technique the metal halides are generated at the sliding surfaces by reaction of nickel- or cobalt-base alloys with halogen-containing gaseous atmospheres.

Figure 2 was constructed from data in reference 3 that give the effect of temperature on the vapor pressures of some halides of interest. At any temperature, CaF_2 has the lowest vapor pressure of the compounds shown.

At 1500° F the vapor pressure of CaF_2 (extrapolated from the data in fig. 2) is about 10^{-7} millimeter of mercury. At 1500° F, the vapor pressure of NiF_2 is about 10^{-2}, of $NiCl_2$ about 30, $NiBr_2$ about 300 millimeters of mercury; and NiI_2 sublimes at 1377° F. According to reference 5, atmospheric pressure is 10^{-7} millimeter at an altitude of about 180 miles. Therefore, a relatively low sublimation rate would be expected for CaF_2 at high temperatures and high altitudes. The high vapor pressures of the nickel and cobalt chlorides and bromides severely limit their usefulness as high-temperature solid lubricants for use in open systems.

Table II gives some of the pertinent properties of the compounds under discussion. At moderate temperatures, experience has shown that low friction coefficients are obtained for metals lubricated with nickel and cobalt chlorides and bromides. This is probably due to their crystal structure, which is similar to that of graphite and MoS_2. It is a laminar, hexagonal structure with easily sheared basal planes. CaF_2 has a cubic structure, but exhibits planes of easy cleavage (111 planes, ref. 6). The MX_2 type composition also may be expected to contribute to a low-shear-strength structure (ref. 7).

FORMULATION AND APPLICATION OF COATINGS

For convenience in discussing the application of ceramic coatings, a number of terms will be used that are common to ceramics but not generally encountered in lubrication technology. A brief glossary is therefore included in the appendix to define a few of these terms as they are to be interpreted for purposes of this report.

Formulation of Coatings

The metal oxide ceramic systems were formulated on the basis of melting point (or softening range), vitrifying tendency, and thermal-expansion coefficient. Melting points several hundred degrees above the maximum use temperature, but below the melting point of the substrate metal, were selected. A "glass-forming" oxide such as B_2O_3 was included to enhance the vitrifying tendency of the ceramic. A vitrification tendency is desirable to promote the formation of a glaze on the wear track of ceramic coating. (The friction and wear of metals in sliding contact with ceramics generally decrease sharply when a glazed wear track forms on the ceramic surface. See refs. 1, 8, and 9.) The compositions were balanced to provide a thermal-expansion coefficient approximating that of the base metal.

Melting points were estimated from the phase diagram for ceramic systems found in reference 10, and approximate thermal-expansion coefficients were calculated from factors found in reference 11.

Preparation of Enamel Frits

The frits were prepared in the following manner. Reagent-grade powders were mixed in the desired proportion and ball-milled to a fine uniform mixture. The mixture was then melted in large porcelain crucibles until a quiescent, uniform melt was obtained. The melt was slowly poured into cold water to form friable shot-like globules, which were filtered, dried, and finally ball-milled to pass a 200-mesh screen.

The preparation of frits is necessary to ensure homogeneity and to exclude all volatiles prior to application of the enamel to a metal. For instance, boric oxide (B_2O_3) is introduced into a ceramic composition by thermal decomposition of boric acid (H_3BO_3) to B_2O_3 and water, thus liberating steam. This reaction causes bubbling in the molten ceramic and would be extremely undesirable if it were allowed to occur during fusion of the coating material to the substrate.

Application of Coatings to a Metal Surface

One hundred grams of frit were suspended in about 750 milliliters of water. The fine powder was violently stirred into a slurry by a high-speed blender. No suspending agents were used, but the solids remained in suspension long enough to be sprayed.

The metal disks were preheated to 500° F immediately before spraying. Upon spraying, the water evaporated from the hot metal, and a thin film of ceramic powder remained. The coating was built up to the desired thickness by repeated passes with the spray gun.

After spraying, the disks were fired at 2000° F to fuse the ceramic to the base metal. Upon removal from the furnace, the specimens were brought to room temperature on a water-cooled steel block.

The ceramic-bonded fluoride coatings were applied in essentially the same way. A measured amount of fluoride was mixed with the ceramic frit, stirred into suspension, and sprayed. The firing temperature of 2000° F was above the melting point of the ceramic but below that of the fluoride. Upon cooling, the ceramic solidified and acted to bind the fluoride particles to each other and to the substrate metal. A CaF_2 overlay was applied to some of the ceramic-bonded CaF_2 coatings in the following manner. A very thin CaF_2 film was sprayed on the coating with an airbrush. This disk was baked at 1700° F for 4 minutes to sinter the CaF_2 particles. A second CaF_2 spray followed by a $2\frac{1}{2}$-minute bake at 1700° F was then applied. Finally, the overlay was burnished on a flannel-covered polishing wheel impregnated with dry CaF_2.

Diffusion-bonded coatings were applied by spraying a slurry of CaF_2 (or SrF_2) and $AlPO_4$ onto the preheated disks and heating to 1700° F to sinter the fluoride particles and to promote diffusion of base-metal oxide throughout the coating.

For all coatings, the thickness was held between 0.001 and 0.002 inch.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used in performing the lubrication studies is shown in figure 3. A detailed description is given in reference 12. Basically, a rotating disk is placed in sliding contact with a hemispherically tipped rider (3/16-in.-rad. hemisphere) under a normal load of 1 kilogram. The rider describes a 2-inch-diameter wear track on the disk. Sliding is unidirectional and at a velocity of 430 feet per minute. Friction torque is measured with strain gages and continuously recorded. All specimens were "run-in" with incrementally increased loads according to the following procedure: 2 minutes at 200 grams, 2 minutes at 400 grams, 2 minutes at 600 grams, 2 minutes at 800 grams, and finally, 1000 grams for the remainder of the test.

Before each test, the rider and disk specimens were cleaned according to the following procedure:

(1) Wash with acetone.

(2) Scrub with levigated alumina (omitted when cleaning disks to avoid embedding alumina particles into coatings).

(3) Rinse with hot tap water.

(4) Rinse briefly with distilled water.

(5) Blot dry with filter paper.

(6) Store in desiccator.

RESULTS AND DISCUSSION

Three general types of coating were investigated, and their lubricating properties were evaluated from 75° to 1500° F. They may be classified as fused ceramic coatings, diffusion-bonded or sintered fluoride coatings, and ceramic-bonded fluoride coatings. Compositions of rider and substrate metals used are given in table III.

Ceramic Coatings

A number of experimental ceramic coatings were formulated. The compositions and lubricating properties of a cobalt oxide (CoO) ceramic and two barium oxide (BaO) ceramics are given in figure 4. The friction and wear of cast Inconel sliding on unlubricated Inconel X and on Inconel X lubricated with the various ceramics are compared. Over the temperature range studied, all three coatings afforded a considerable reduction in rider wear compared with the unlubricated metals. Friction coefficients were 0.2 or higher in all cases. The CoO coating was perhaps the most interesting because it was the only one that gave a friction coefficient less than 0.4 at all test temperatures. This coating could be useful for high-temperature application in which wear reduction is a prime concern and fairly high friction coefficients can be tolerated. The maximum acceptable friction coefficient for boundary lubrication is usually given as 0.2. The values for this coating ranged from 0.24 to 0.36.

Diffusion-Bonded Fluoride Coatings

In an attempt to obtain lower friction coefficients, coatings of metal halides were considered. Since the thermal-stability studies had indicated that CaF_2 and SrF_2 were quite stable in air up to at least 2000° F, coatings containing these compounds were developed and their lubricating properties were evaluated.

Table IV(a) gives the results of friction and wear tests obtained with SrF_2 coatings containing 10 percent aluminum phosphate ($AlPO_4$). At 1500° F, the friction coefficient was 0.10, but the coating failed in a very short time. The failure point was taken as the time at which the friction coefficient became erratic and increased in magnitude.

Figure 5 gives the friction coefficients obtained with cast Inconel sliding on Haynes Stellite 21 and on Inconel X lubricated with CaF_2 coatings containing 10 percent $AlPO_4$. At 1500° F, friction coefficients below 0.2 were obtained in some cases. Prolonged baking at 1500° to 1700° F prior to testing improved the endurance life characteristics of the coatings.

The beneficial effect of prolonged high-temperature baking appears to be attributable to the fact that high temperature promotes solid-state diffusion. This has two important effects: First, sintering of the individual fluoride particles into a more coherent film is likely, and second, oxides generated by oxidation of the metal surface at the ceramic-metal interface diffuse throughout the coating. During the high-temperature bake, an increase in the chromium oxide (Cr_2O_3) and possible NiO content of the coating is easily observed as the color of the coating gradually changes from pure white to green. The presence of a tenacious oxide film at the coating-metal interface and the penetration of this oxide throughout the entire thickness of the coating may contribute to improved adherence and endurance properties.

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The diffusion-bonded fluoride class of coatings was studied in only a preliminary manner. It was tentatively assumed that a more practical approach would be to develop a class of coatings with a more positive bonding mechanism - a mechanism in which the bond strength would depend primarily upon the initial firing of the coating on the substrate metal, and not upon subsequent exposure time to temperature up to the maximum test temperature (1500° F).

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Ceramic-Bonded Fluoride Coatings

To obtain more positive bonding, the CoO-base ceramic previously described was selected as a binder for CaF_2 and SrF_2 coatings. SrF_2 and CaF_2 coatings containing various percentages of binder were evaluated. The data of table IV(b) indicate that SrF_2 coatings show little promise as solid lubricants.

Figures 6(a) and (b) give the effect of binder to fluoride ratio on the friction coefficients and endurance characteristics of CaF_2 coatings at 500°, 1000°, 1200°, and 1500° F. In general, the best results were obtained with the composition containing 25 percent binder (3 to 1 lubricant to binder ratio). This composition did not fail in 50,000 cycles (1 hr) except at 1500° F. No attempt was made here to determine the endurance limit of these coatings. For present purposes, coatings that survived a 1-hour test (50,000 cycles) were considered to have acceptable endurance lives.

The results of a more detailed study of the lubricating properties of the CaF_2 coating with 25 percent binder are given in figure 7. The highest friction coefficient obtained was 0.26 at 75° F. The friction coefficient gradually decreased with temperature to 0.11 at 1200° F, then increased to an average value of about 0.15 at temperatures between 1300° and 1500° F. Rider wear was low at all temperatures compared with the wear obtained with unlubricated metals, but it was considerably greater at 1500° F than at the lower temperatures.

Increased wear and decreased endurance at 1500° F were not considered inherent characteristics of CaF_2. They could be caused by some undesirable physical property of the coating such as porosity, which could be expected to contribute to poor strength properties. Porosity was reduced by sintering and then burnishing a very thin CaF_2 layer on the surface of the coating. The effect of this procedure was to fill the microscopic voids in the surface with CaF_2.

The data of figure 7 show that the overlay had no significant effect on the friction coefficient or rider wear at 1200° and 1350° F. However, at 1500° F the effect of the overlay was to reduce the friction coefficient from 0.15 to about 0.06. Rider wear rate was reduced to about one-tenth that obtained without the overlay. Table V shows that coatings without a CaF_2 overlay failed before 50,000 cycles at temperatures above 1300° F, but those with the overlay did not fail in 50,000 cycles at 1300° and 1500° F. For purposes of comparison, the lubrication properties of a PbO coating (ref. 1) are given in figure 7. This coating cannot be used above about 1250° F because it melts at about 1300° F.

Figure 8 gives the effect of temperature cycling on the friction coefficient of a CaF_2 coating with 25 percent binder and a sintered CaF_2 overlay. The test was started at 650° F and the temperature was increased to 1500° F, then allowed to decrease to room temperature. The specimens were run for short time intervals at the temperatures indicated by the data points, then stopped. This was done because of the long time required to heat and cool the test apparatus over the indicated temperature range. The curve essentially duplicates that of figure 7 where different specimens were used for each data point. It confirms the conclusion drawn from the data of figure 7 that the overlay produces a significant decrease in friction from about 1350° to 1500° F but has no appreciable effect on friction at lower temperatures.

SUMMARY OF RESULTS

This investigation was concerned with the formulation, application, and evaluation of dry film lubricants for temperatures up to 1500° F. Thermodynamic properties were among the main considerations in selecting materials for study. The major results of this investigation were:

1. Of the various coatings investigated, the best overall lubricating effectiveness from 75° to 1500° F was obtained with a ceramic-bonded CaF_2 coating on an Inconel X substrate. CaF_2 coatings containing 25 percent binder gave friction coefficients of 0.26 at 75° F, 0.20 at 500° F, and 0.15 at 1500° F. The addition of a thin surface film of pure CaF_2 reduced the friction coefficient at 1500° F to 0.06, but gave the same friction coefficients as coatings without the overlay from 75° to 1350° F.

2. In the temperature range from 75° to 1500° F, several experimental ceramic coatings provided appreciable reduction in rider wear compared with that obtained with unlubricated metals. Friction coefficients, however, ranged from about 0.3 to 0.4. One of these ceramic compositions, containing CoO as the main ingredient, was effectively employed as the binder in ceramic-bonded CaF_2 coatings.

3. The thermodynamic properties of the halides and oxides were very useful in selecting materials that would be chemically stable in air at high temperatures. Thermochemical calculations indicated that only a few of the many halides were sufficiently stable to merit detailed investigation. Among these, CaF_2 has so far been the most effective as the main component in a dry film lubricant. In addition to good thermal stability, CaF_2 has the desirable properties of low vapor pressure, low water solubility, and a readily sheared crystal structure.

Lewis Research Center
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APPENDIX - GLOSSARY OF TERMS

Enamel: A thin ceramic coating, usually of high glass content, applied to a substrate, generally a metal.

Frit: A powdered ceramic prepared by fusing a physical mixture of oxides into a uniform melt, which is then quenched and milled into a fine, homogeneous powder.

Fused ceramic: A ceramic body or coating prepared by heating ceramic powders above the melting point, then cooling to form a coherent mass or film.

Sintered ceramic: A ceramic body or coating prepared by heating a ceramic powder below its melting point but at a sufficiently high temperature to cause interdiffusion of ions between contacting particles and subsequent adherence at the points of contact.

Slip: A sprayable slurry prepared from a frit suspended in a liquid carrier (sometimes also used for dip and brush coating).

Softening range: An arbitrarily defined temperature range below the crystal melting point where a ceramic becomes soft and noticeably viscous; a softening range rather than a sharp melting point occurs in ceramics containing a glass phase.

Vitrifying tendency: Tendency of the crystalline phase of a ceramic to transform into an amorphous or glassy phase when subjected to aging or temperature cycling.

REFERENCES

1. Johnson, R. L., and Sliney, H. E.: High-Temperature Friction and Wear Properties of Bonded Solid Lubricant Films Containing Lead Monoxide. Lubrication Eng., vol. 15, no. 12, 1959, pp. 487-491; 496.

2. Glassner, A.: The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500° K. ANL-5750, AEC, 1957.

3. Quill, Laurence L.: The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics. McGraw-Hill Book Co., Inc., 1950.

4. Buckley, Donald H., and Johnson, Robert L.: Halogenated Gases for High Temperature Lubrication of Metals. Ind. and Eng. Chem., vol. 51, no. 5, May 1959, pp. 699-700.

5. Kallmann, H. K., and Juncosa, M. L.: A Preliminary Model Atmosphere Based on Rocket and Satellite Data. RM-2286, Rand Corp., Oct. 30, 1958.

6. Winchell, Alexander Newton: The Microscopic Character of Artificial Inorganic Solid Substances of Artificial Minerals. John Wiley & Sons, Inc., 1931.

7. Peterson, M. B., and Johnson, R. L.: Factors Influencing Friction and Wear with Solid Lubricants. Lubrication Eng. vol. 11, no. 5, Sept.-Oct. 1955, pp. 325-331.

8. Herron, R. H.: Friction Materials - A New Field for Ceramics and Cermets. Am. Ceramic Soc. Bull., vol. 34, no. 12, Dec. 1955, pp. 395-398.

9. Coes, L., Jr.: Chemistry of Abrasive Action. Ind. and Eng. Chem., vol. 47, no. 12, Dec. 1955, pp. 2493-2494.

10. Levin, Ernest M., McMurdie, Howard F., and Hall, F. P.: Phase Diagrams for Ceramists. The Am. Ceramic. Soc., Inc., 1956.

11. Andrews, A. I.: Enamels. The Twin City Printing Co., Champaign (Ill.), 1935.

12. Sliney, Harold E.: Effect of Sliding Velocity on Friction Properties and Endurance Life of Bonded Lead Monoxide Coatings at Temperatures up to 1250° F. NACA RM E58B11, 1958.

13. Hodgman, Charles D., ed.: Handbook of Chemistry and Physics. Thirty-eighth ed., Chem. Rubber Pub. Co., 1956-1957.

14. Wyckoff, Ralph W. G.: Crystal Structures. Vol. I. Interscience Pub., Inc., 1948.

TABLE I. - THERMAL STABILITIES OF SOME METAL HALIDES IN AIR

[Powders of the compounds were contained in ceramic boats and exposed to the indicated temperatures for 1 hour, then cooled in a desiccator. See footnote for exceptions. Compounds are listed in order of decreasing stability in air.]

Compound	Temperature, °F	Compounds detected by X-ray diffraction after test (a)	Appearance after test
SrF_2	2000	SrF_2	Powders sintered into a porous mass
CaF_2	2000	CaF_2	Same results as SrF_2
$NiF_2 \cdot 4\ H_2O$	75	$NiF_2 \cdot 4\ H_2O$	Light green powder
	500	NiF_2	Bright yellow powder
	750	NiF_2 (W)	Greenish-yellow powder
	1000	NiO (W)	Olive-drab powder
$CoCl_2 \cdot 3\frac{1}{2}\ H_2O$	75	$CoCl_2 \cdot 3\frac{1}{2}\ H_2O$	Deep red powder
	500	$CoCl_2$	Bright blue powder
	750	$CoCl_2$ + small amount Co_3O_4	Bright blue with black powdery surface layer
	1000	$CoCl_2 + Co_3O_4$ (approx. equal amounts)	Bright blue powder under thick black layer
	1300	Co_3O_4	Black powder
$FeCl_2 \cdot 4\ H_2O$	75	$FeCl_2 \cdot 4\ H_2O$	Brown powder
	500	$FeCl_2 \cdot 2\ H_2O$ + small amount Fe_3O_4	Dark brown powder
	750	Fe_2O_3	Dark red powder
$NiCl_2 \cdot 6\ H_2O$	75	$NiCl_2 \cdot 6\ H_2O$	Emerald-green powder
	500	$NiCl_2$ (W)	Tan to yellow powder
	750	$NiCl_2$ (W)	Tan to yellow powder
	1000	NiO	Olive-drab powder
$NiBr_2$	[b]250	$NiBr_2$ + NiO	Tan coating
	[b]500	NiO	Olive-drab coating
	[b]1000	NiO	Olive-drab coating

[a]W signifies "weak" intensity of diffraction pattern, may indicate presence of amorphous Ni_3O_4, which would dilute crystalline phases identified.

[b]These samples were exposed to air at the indicated temperatures as thin films (0.002 in.) on Inconel.

TABLE II. - PHYSICAL PROPERTIES OF SOME METAL HALIDES OF INTEREST AS EXPERIMENTAL SOLID LUBRICANTS

Compound	Melting point, °F	Solubility, g/100 ml		Crystal data (a)	References
		Cold water	Hot water		
CaF_2	2583	-------------- 0.0016 (18° C) --------------	-------------- 0.0017 (26° C) --------------	------------------ ------------------ Cubic with perfect (111) cleavage planes	3 13 6
SrF_2	2552	-------------- 0.011 (0° C) --------------	-------------- 0.012 (27° C) --------------	------------------ ------------------ Cubic (isometric with CaF_2 lattice)	3 13 6
NiF_2	1881	-------------- --------------	-------------- --------------	---------- Tetragonal	3 14
CoF_2	2196	-------------- --------------	-------------- --------------	---------- Tetragonal	3 14
FeF_2	2012	-------------- --------------	-------------- --------------	---------- Tetragonal	3 14
$NiCl_2$	Sublimes 1809	-------------- 64.2 (20° C) --------------	-------------- 87.6 (100° C) --------------	--------- --------- Hexagonal	3 13 14
$CoCl_2$	1341	-------------- 45 (7° C) --------------	-------------- 105 (96° C) --------------	--------- --------- Hexagonal	3 13 14
$FeCl_2$	1251	-------------- 64.4 (10° C) --------------	-------------- 105.7 (100° C) --------------	--------- --------- Hexagonal	3 13 14
$NiBr_2$	Sublimes 1611	-------------- 112.8 (0° C) --------------	-------------- 155.1 (100° C) --------------	--------- --------- Hexagonal	3 13 14
NiI_2	Sublimes 1377	-------------- 124.2 (0° C) --------------	-------------- 188.2 (100° C) --------------	--------- --------- Hexagonal	3 13 14

[a]Hexagonal crystal structures for MX_2 compounds often have low shear strength and a low friction coefficient because of relatively low bond energies between the basal planes of the hexagonal platelets. Cubic and tetragonal crystal structures are not generally associated with low shear strength, but perfect cleavage planes as in CaF_2 might contribute to an easily sheared structure suitable for use as a solid lubricant.

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TABLE III. - NOMINAL CHEMICAL COMPOSITIONS OF ALLOYS USED IN THIS INVESTIGATION

Alloy	Chemical composition, weight-percent											
	Ni	Co	Cr	Fe	C	Si	Mo	Al	Mn	Cu	Nb	Ti
Cast Inconel	Balance	----	13.5	6	0.2	2	--------	---	0.8	0.25	--	---
Inconel X	Balance	----	15	7	0.4	0.4	--------	0.7	0.5	0.2	1	2.5
HS-21	1.5-3.5	Bal-ance	25-30	2.0	0.3	---	4.5-6.5	---	---	---	--	---

TABLE IV. - LUBRICATING PROPERTIES OF STRONTIUM FLUORIDE COATINGS

[Sliding velocity, 430 ft/min; load, 1 kg; rider, cast Inconel with 3/16-in.-rad. hemispherical tip; disk, Inconel X.]

(a) With $AlPO_4$

Coating	Test temperature, °F	Friction coefficient	Rider wear rate, cu in./hr
SrF_2 plus 10 percent $AlPO_4$ (as sprayed)	1500	0.10	Coating failed in 3 min
SrF_2 plus 10 percent $AlPO_4$ (diffusion-bonded 1 hr at 1700° F)	1500	----	Coating failed immediately

(b) With ceramic binder

Coating	Test temperature, °F	Friction coefficient	Rider wear rate, cu in./hr
SrF_2 plus 10 percent ceramic binder	500 1000 1450	0.24 .30 .14	1.78×10^{-6} Coating failed in 5 min Coating failed in 13 min
SrF_2 plus 25 percent ceramic binder	500 1500	0.32 .37	34.0×10^{-6} 236×10^{-6}

TABLE V. - ENDURANCE PROPERTIES OF CERAMIC-BONDED CALCIUM FLUORIDE

COATINGS WITH AND WITHOUT CALCIUM FLUORIDE OVERLAY

[Sliding velocity, 430 ft/min; load, 1 kg; binder, 25 percent enamel; base metal, Inconel X; rider material, cast Inconel ground to a 3/16-in. rad. at one end.]

Temperature, °F	Without overlay		With overlay	
	Av. cycles to failure, revolutions	Number of tests	Av. cycles to failure, revolutions	Number of tests
75	6.5×10^3	2		
250	11.0×10^3	2		
500	No failure at 50×10^3	2		
750	No failure at 50×10^3	1		
1000	No failure at 50×10^3	2		
1200	No failure at 50×10^3	2	No failure at 50×10^3	1
1300	48.0×10^3	1	No failure at 50×10^3	1
1350	47.0×10^3	2		
1430	33.0×10^3	2		
1460	14.0×10^3	1		
1500	17.5×10^3	2	No failure at 50×10^3	3

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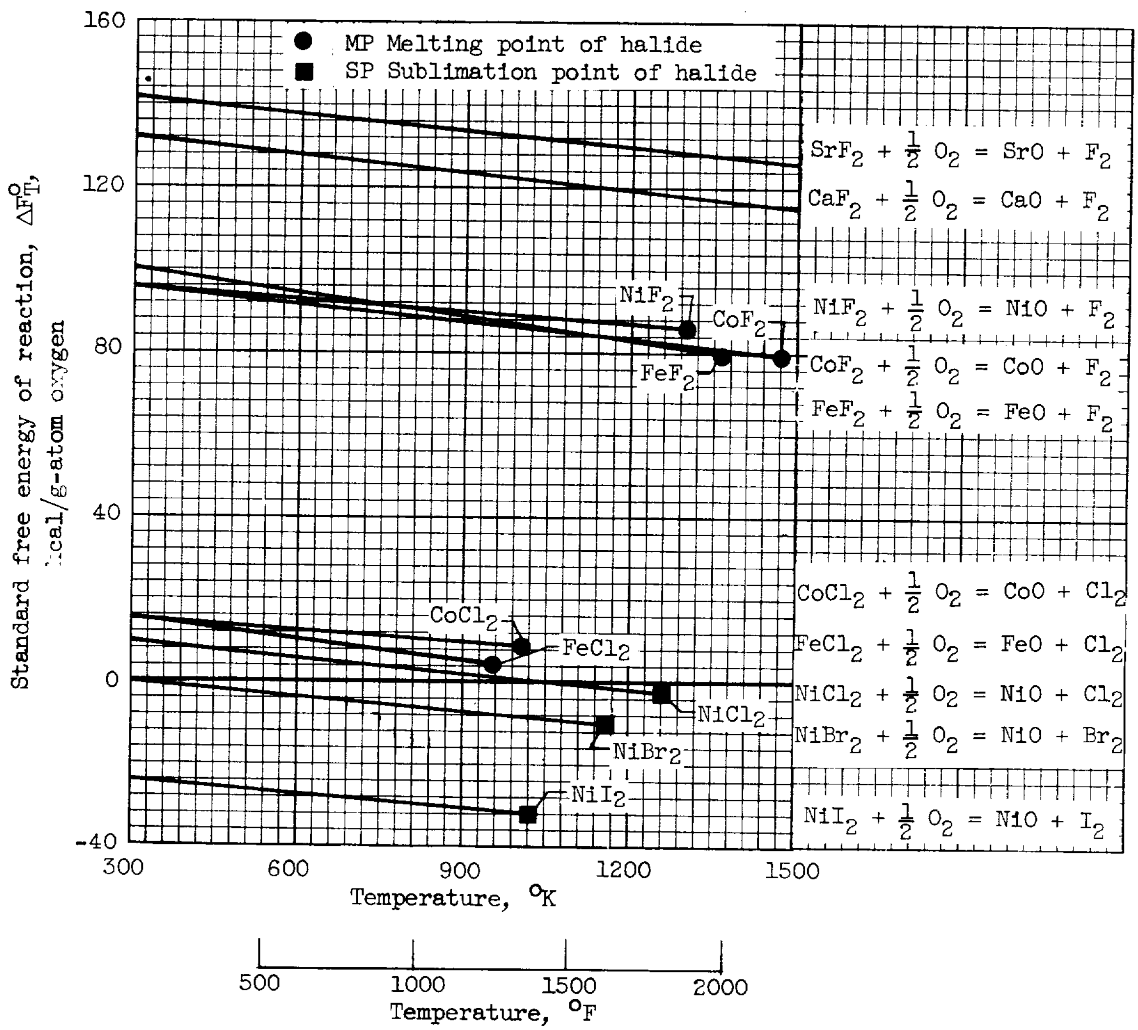


Figure 1. - Thermal stability of some metal halides of interest as experimental solid lubricants. The relative positions of the curves give the order of thermodynamic stability of the halides to which they correspond. Positive ΔF_T^o values indicate the halide will not react with oxygen to form the oxide under standard conditions. Negative ΔF_T^o values indicate the halide will tend to form the oxide. (Standard conditions are partial pressures of gaseous phases involved in reaction equal to unity.)

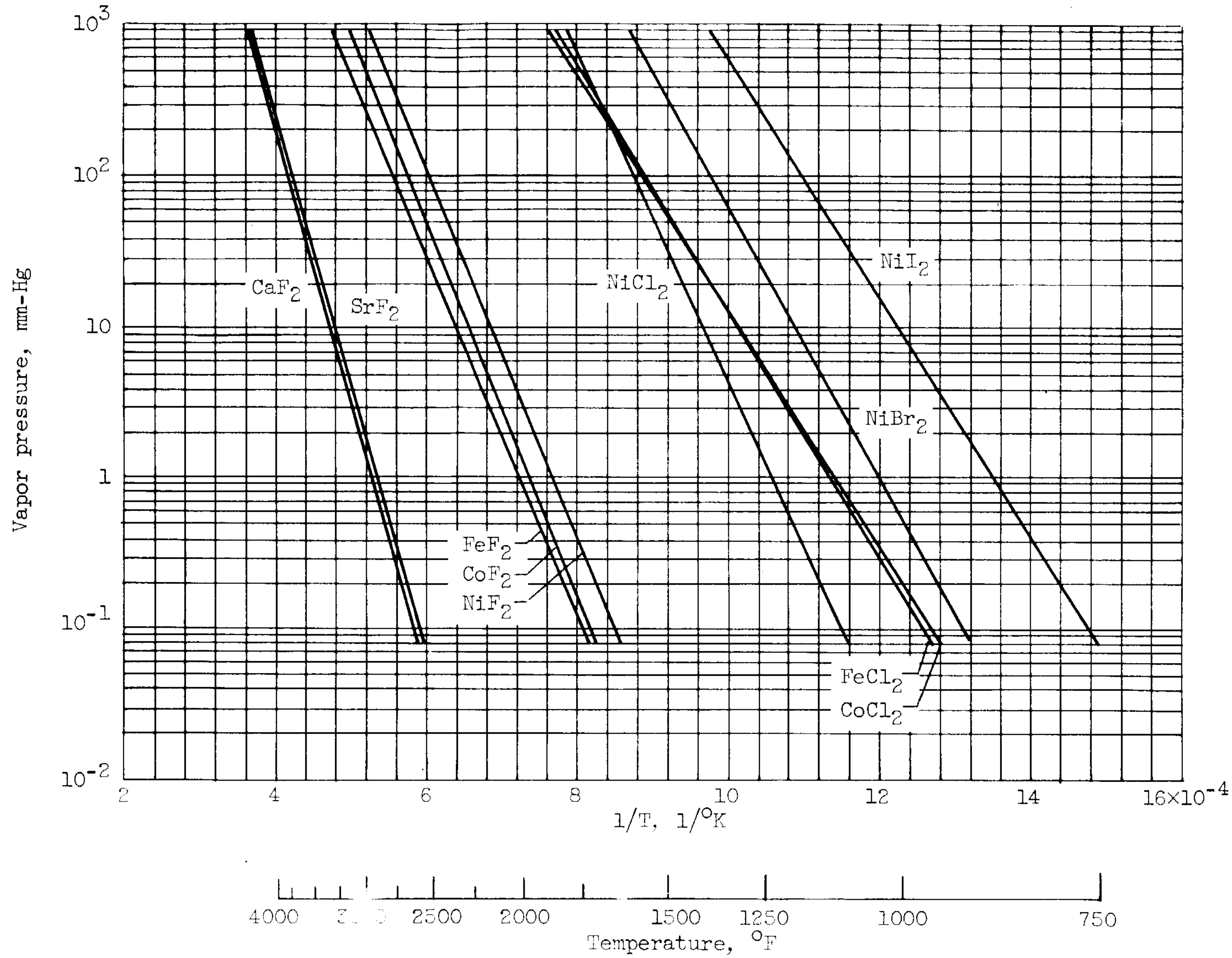


Figure 2. - Effect of temperature on vapor pressures of some metal halides of interest as experimental solid lubricants.

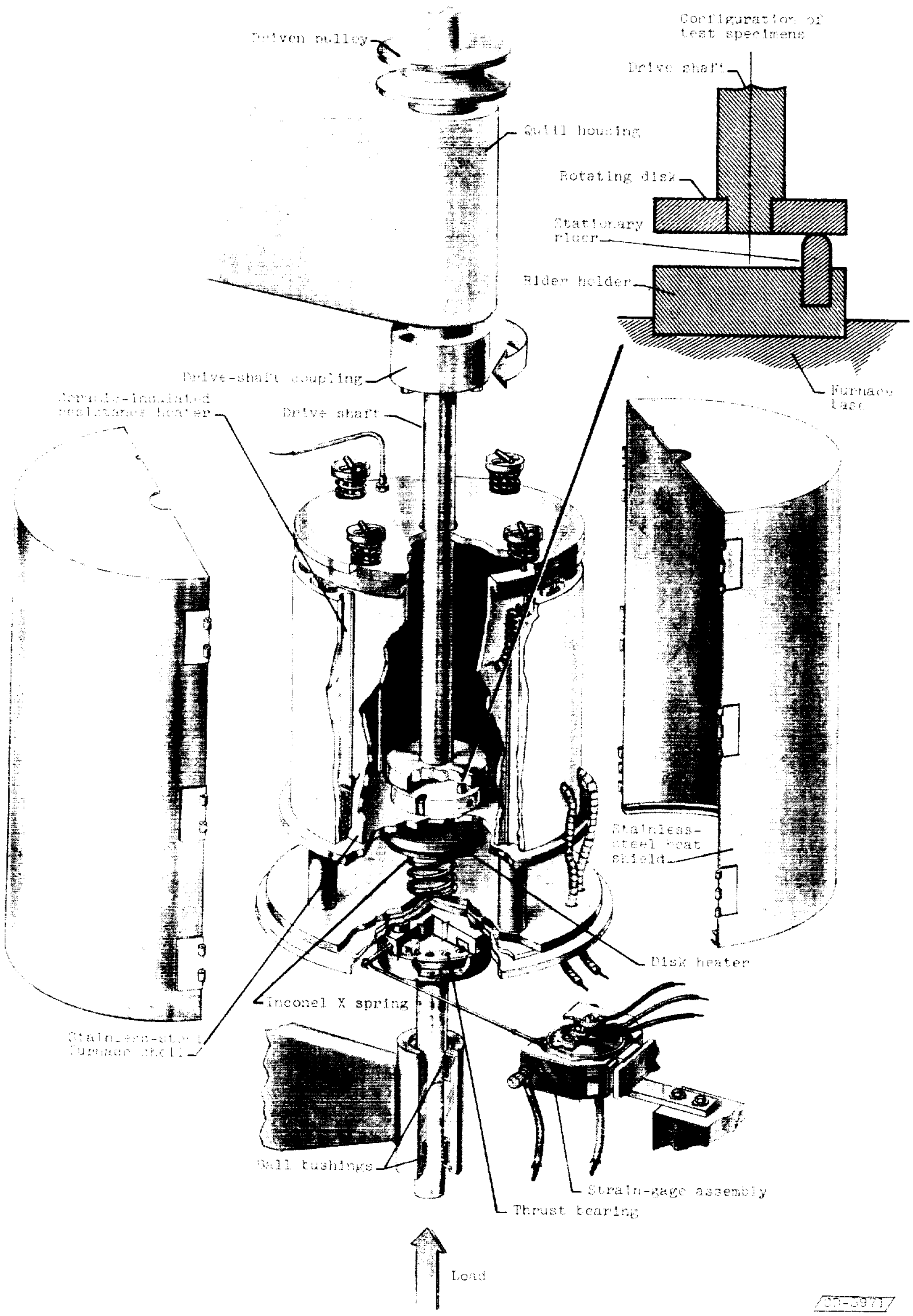


Figure 3. - Apparatus.

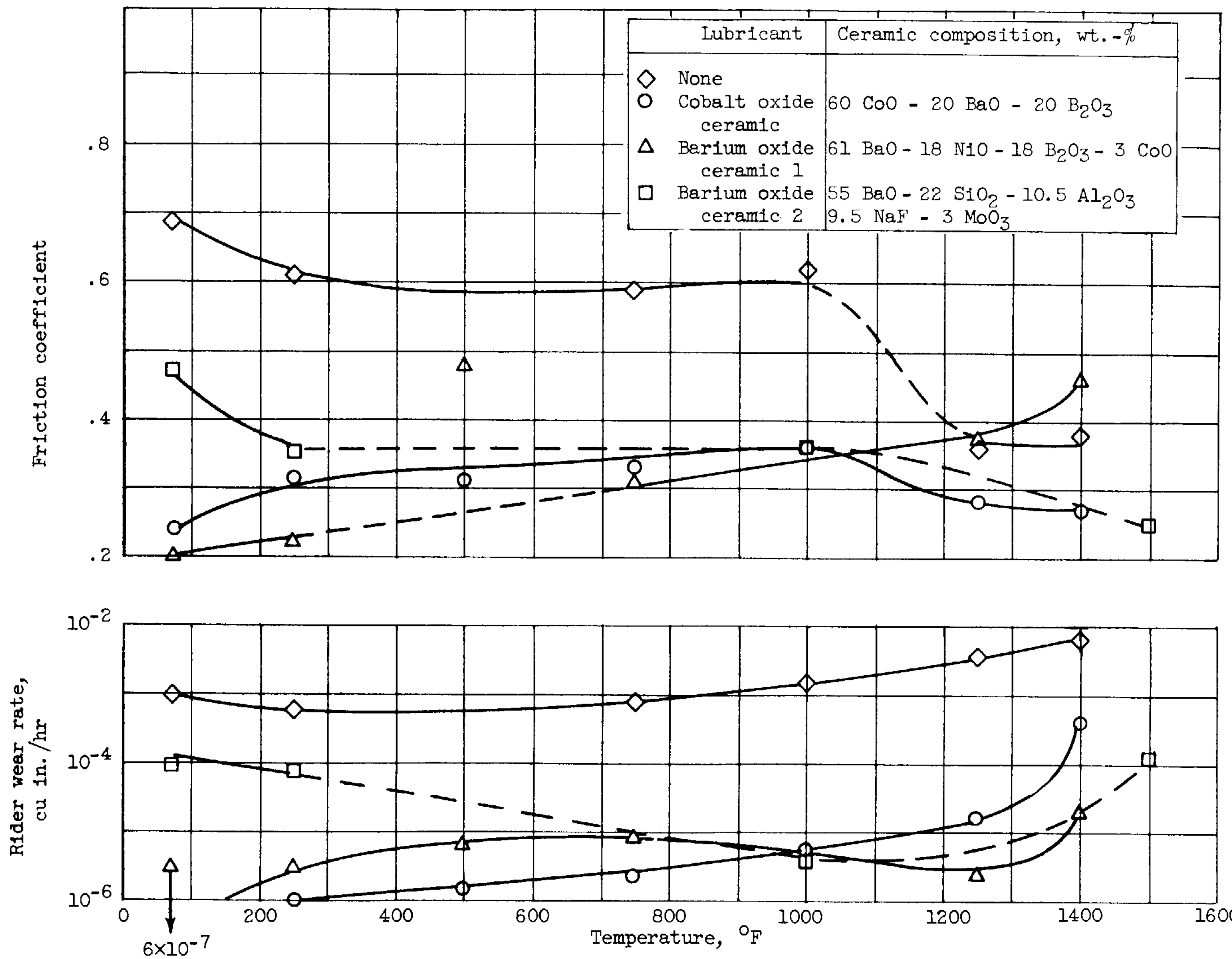


Figure 4. - Effect of temperature on lubricating properties of some experimental ceramic coatings. Coating thickness, 0.001 to 0.002 inch; base metal, Inconel X; rider, cast Inconel (3/16-in.-rad. hemisphere); sliding velocity, 430 feet per minute; load, 1 kilogram.

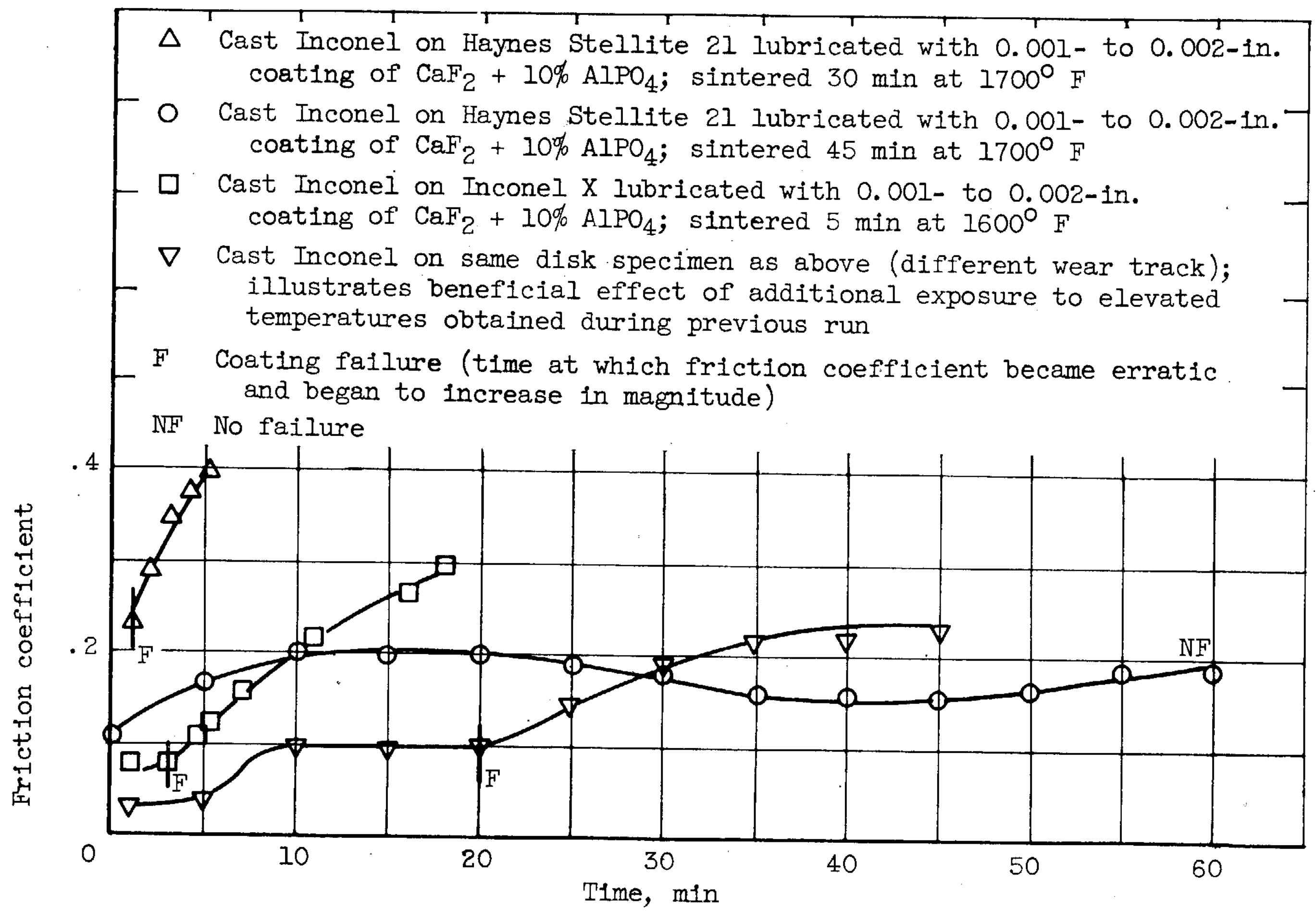
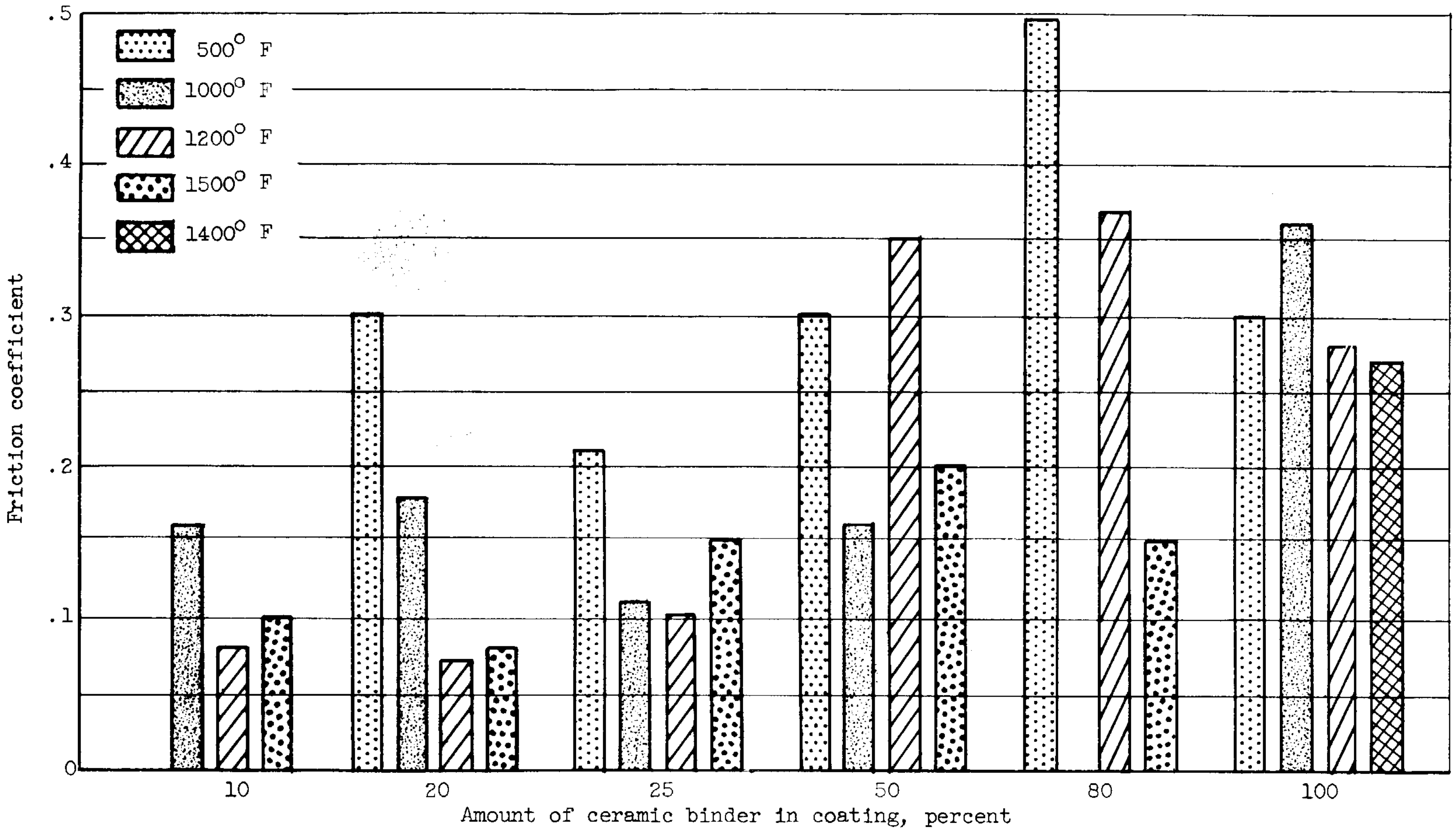
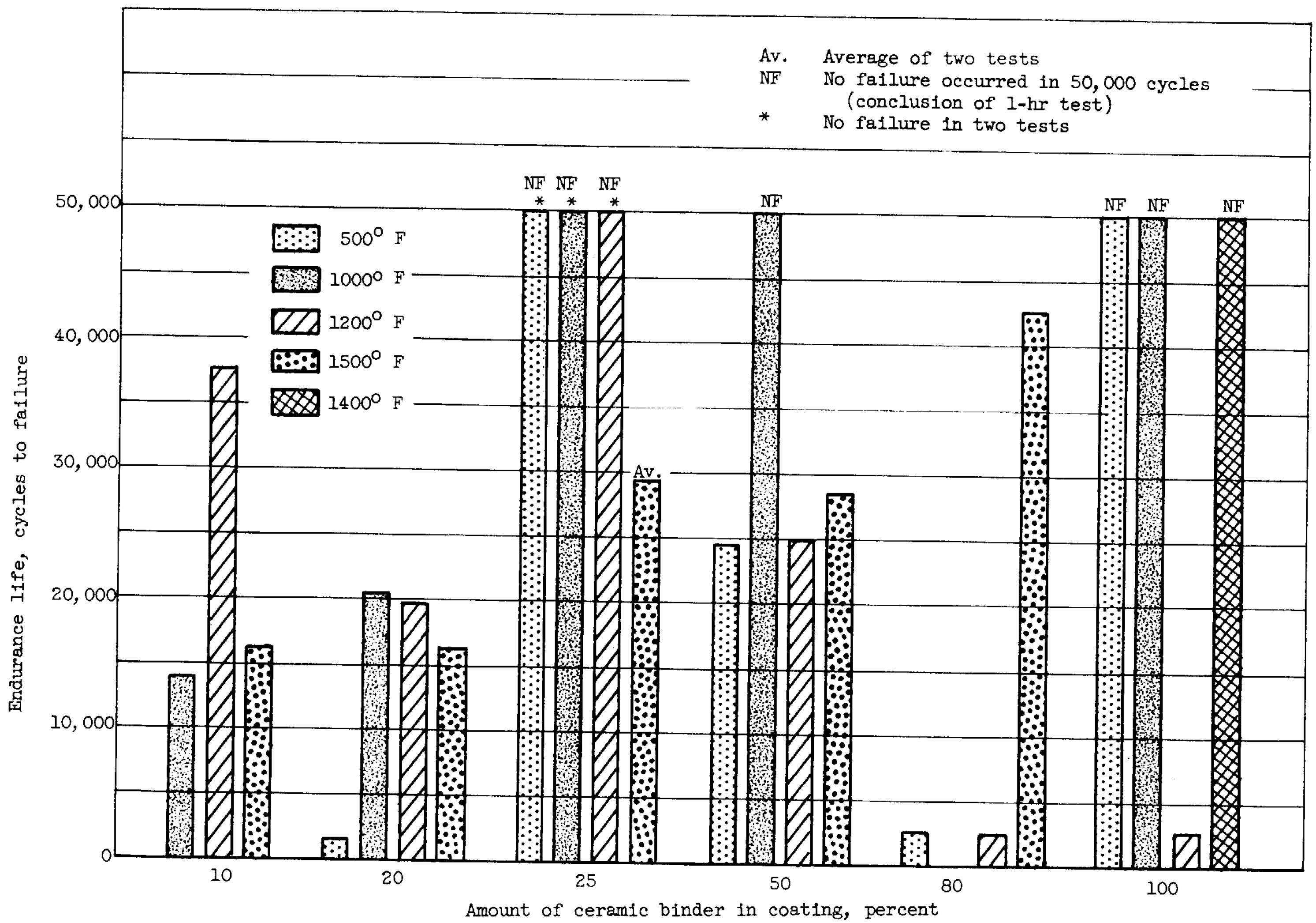


Figure 5. - Lubricating properties of diffusion-bonded calcium fluoride coatings at 1500° F. Effect of bake time and temperature is illustrated. Test conditions: sliding velocity, 430 feet per minute; load, 1 kilogram; rider configuration, 3/16-inch-radius hemisphere.



(a) Friction.

Figure 6. - Effect of ceramic content on lubricating properties of ceramic-bonded CaF_2 coatings on Inconel X. Binder composition, 60% CoO - 20% B_2O_3 - 20% BaO; coating thickness, 0.001 to 0.002 inch; rider material, cast Inconel with 3/16-inch-radius ground on sliding surface; sliding velocity, 430 feet per minute; load, 1 kilogram.



(b) Endurance.

Figure 6. - Concluded. Effect of ceramic content on lubricating properties of ceramic-bonded CaF_2 coatings on Inconel X. Binder composition, 60% CoO - 20% B_2O_3 - 20% BaO; coating thickness, 0.001 to 0.002 inch; rider material, cast Inconel with 3/16-inch-radius ground on sliding surface; sliding velocity, 430 feet per minute; load, 1 kilogram.

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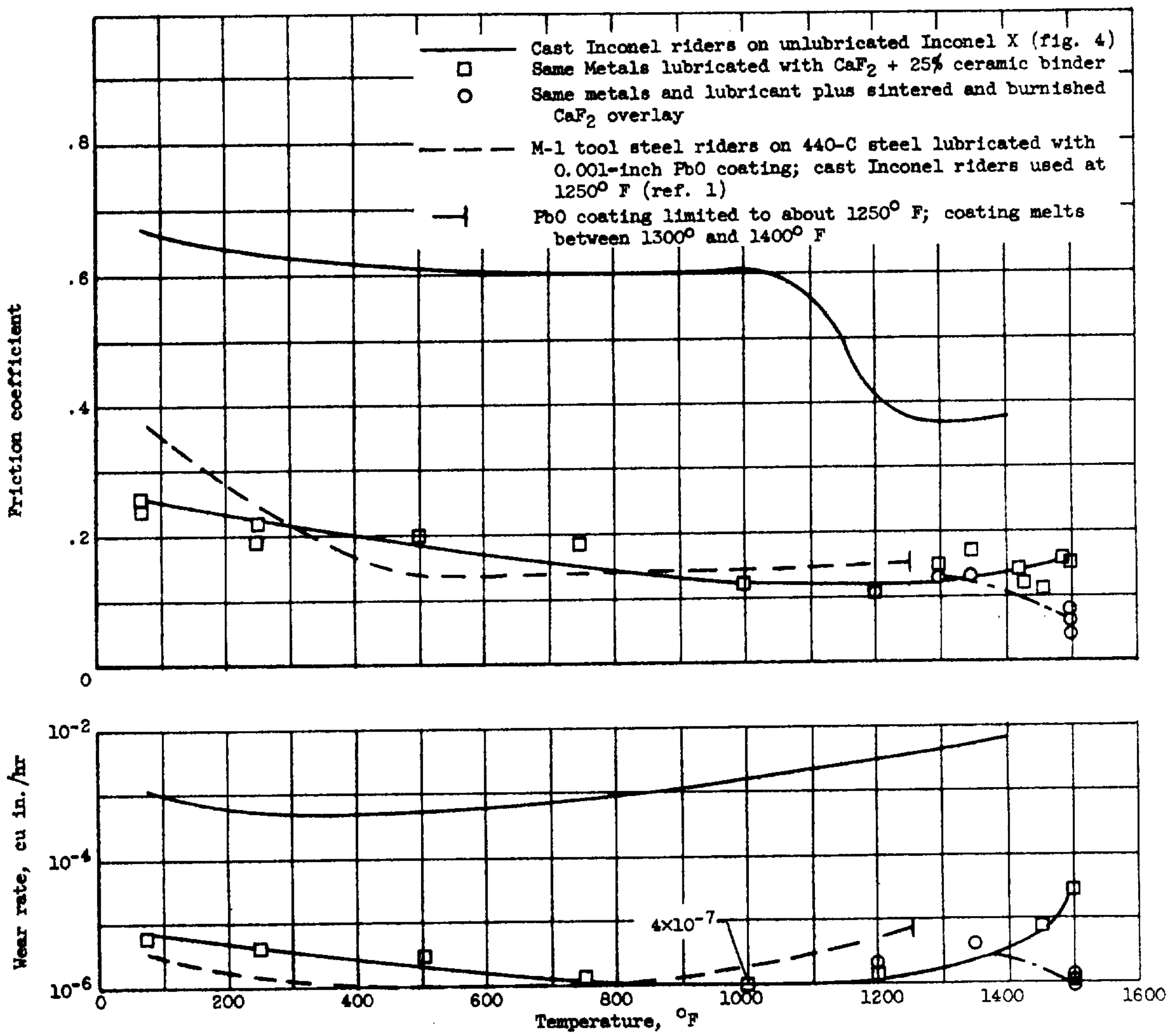

Figure 7. - Effect of temperature on lubricating properties of ceramic-bonded calcium fluoride coatings. Coating thickness, 0.001 to 0.002 inch; rider configuration, 3/16-inch-radius hemisphere; sliding velocity, 430 feet per minute; load, 1 kilogram.

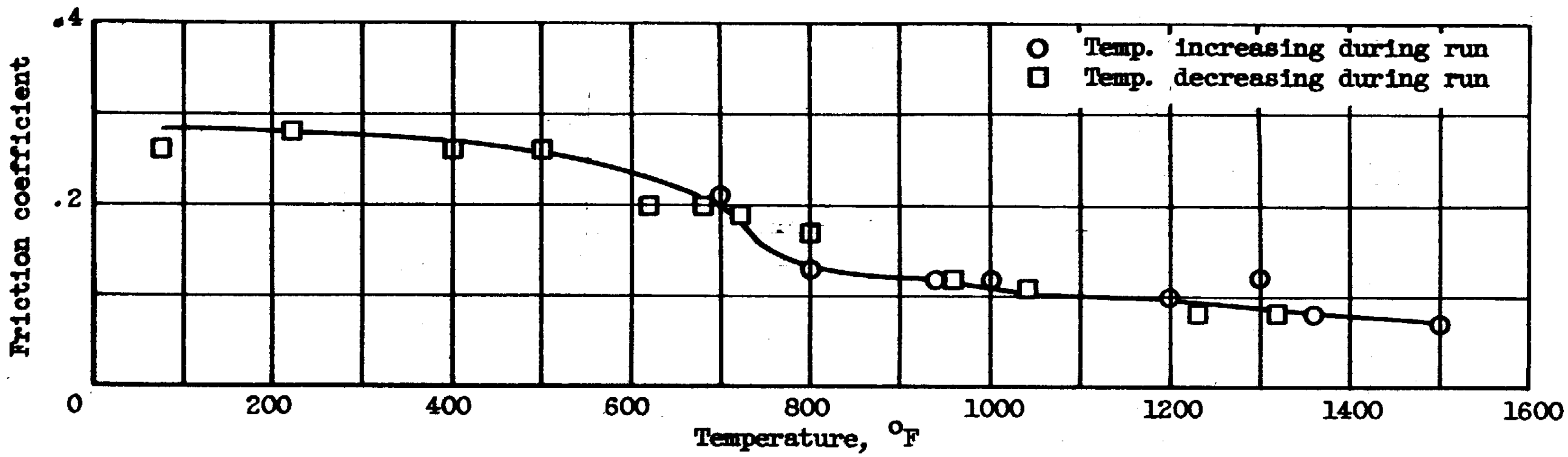

Figure 8. - Friction coefficient of ceramic-bonded calcium fluoride coating subjected to temperature cycling during friction experiment. Coating thickness, 0.001 to 0.002 inch; ceramic content, 25 percent; overlay, sintered and burnished CaF_2 film; base metal, Inconel X; rider material, cast Inconel (3/16-in.-rad. hemisphere); sliding velocity, 430 feet per minute; load, 1 kilogram.

NASA TN D-478
National Aeronautics and Space Administration.
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(NASA TECHNICAL NOTE D-478)

Solid-lubricant coatings, with good chemical stability in air to at least 1500° F, were formulated. Friction and wear data were obtained with hemispherical specimens sliding at 430 ft/min against rotating disks coated with the experimental lubricants. Several ceramic coatings provided moderate friction coefficients (0.3 typical) and prevented severe metal galling and wear. Ceramic-bonded CaF_2 coatings provided low friction coefficients (0.06 at 1500° F, 0.12 at 1000° F) as well as good wear protection at elevated temperatures. The relative thermal stabilities of metal halides in air were estimated by thermochemical calculations and checked by X-ray diffraction.

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